



DESCRIPTION

THERMOELECTRIC CONVERSION MATERIAL, THERMOELECTRIC
CONVERSION DEVICE AND MANUFACTURING METHOD THEREOF

5

TECHNICAL FIELD

The present invention relates to a thermoelectric conversion material having a novel structure and a manufacturing method thereof. More particularly, it relates to a novel structure of a thermoelectric conversion material ~~of a novel structure~~ that has a high thermoelectric figure of merit in a thermoelectric conversion device ~~that~~, which converts heat to electricity or converts
15 electricity to heat, and also to a manufacturing method thereof.

BACKGROUND ART

It is well known that if a thermoelectric
20 conversion material, such as bismuth (Bi), bismuth telluride (BiTe) or silicon-germanium (SiGe), has a low dimensional structure, such as a superlattice structure or nano-wire structure (quantum wire structure), it will have a larger thermoelectric
25 figure of merit Z than it would have in a bulk form (Hicks, L.D., Dresselhaus, M.S., Phys. Rev. B., Vol. 47, 12727(1993)). One main reason ~~effor~~ for this is that a low dimensional structure of the material provides a quantum effect and increases the interface, which
30 leads to a modified density of state and a modified

phonon scattering without a substantial change in resistivity, resulting in a higher Seebeck coefficient α and a lower thermal conductivity than in a bulk ~~form~~ material. In particular, a
 5 thermoelectric material in a nano-wire form has a largely modified density of state (i.e., increase in density of state at band edge) due to the quantum effect. Therefore, and hence this material can have a larger thermoelectric figure of merit than ~~in~~ a two-
 10 dimension structure, such as a super-lattice structure.

The figure of merit ~~Z that~~, which is commonly used as an index of a thermoelectric material, is defined as follows:

$$15 \quad Z = \alpha^2 / \chi \rho \quad (1),$$

where α represents a Seebeck coefficient; χ represents a thermal conductivity; ρ represents a ~~resistivity~~ resistivity. As ~~seen from~~ shown by the equation, an increase in the Seebeck coefficient α or
 20 a decrease in the thermal conductivity χ leads to an increase in the figure of merit Z .

Accordingly, ~~for increasing~~ to increase the Z value, attempts have been made to produce various thermoelectric materials (semiconductor materials) in
 25 a nano-wire form (quantum wire form). For example, an attempt has been made to produce a nano-wire of a thermoelectric material, such as BiTe, BiSb or Bi, by filling pores in a porous oxide film formed by anodization of aluminum (anodized alumina) with ~~such~~

at this material (BiTe, BiSb or Bi) (Amy L. Prieto, Melissa S. Sander, Marisol S. Martin-Gonzalez, Ronald Gronsky, Timothy Sands, and Angelica M. Stacy "J. Am. Chem. Soc." Vol.123, 7160-7161(2001)).

5 ~~Here, an~~ The anodization of aluminum will now be briefly described. In an aluminum anodization process ~~of aluminum, an~~ anodizing aluminum plate or aluminum film formed on a substrate in an electrolyte acid produces porous oxide film (anodized alumina)
 10 (RC. Furneaux, W. R. Rigby & A. P. Davidson "Nature" Vol. 337, P147 (1989)). ~~This~~ The characteristic geometrical feature of the porous oxide film is ~~characterized by the geometrical feature that fine cylindrical pores of diameters of several nanometers~~
 15 to several hundred nanometers (nano-holes) in diameter are arranged in parallel ~~at spacing of,~~ spaced apart by several tens nanometers to several hundred nanometers (cell sizes). Cylindrical pores ~~these arranged at spacing of~~ spaced apart by at least
 20 several tens ~~nanometer or more~~ of nanometers have a high aspect ratio and a relatively uniform cross sectional diameter. The diameter and spacing of the pores can be controlled to a certain degree by properly selecting the acid species and the voltage
 25 for anodization.

 Thus, such anodized aluminum oxide film ~~of aluminum~~ can be used as a mold to produce a thermoelectric material in a nano-wire form, which will increase the figure of merit Z.

30 However, in the anodization process of aluminum,

when the anodization voltage is adjusted to form pores at spacing of 10 nm or less, so as to obtain nano-wires at a high density, it is difficult to form adjacent pores separated from each other by an

5 anodized alumina wall 93 on a substrate 94 as shown in Fig. 9, ~~that is~~ 9; i.e., pores tend to communicate with each other. In this situation, the anodized alumina 93 contains a ~~more~~ greater number of non-isolated pores 92 than isolated pores 91. Thus, it

10 is difficult to produce pores separated by alumina walls ~~with spacing of that~~ are spaced apart by 10 nm or less, and a large area is required to produce a large number of nano-wires.

According to a theoretical calculation, the

15 smaller the size (diameter) of the nano-wire is, the greater the figure of merit ~~Z becomes~~. However, the anodization of aluminum can only produce pores or nanowires ~~of a size (diameter) of that are~~ about 7 to 9 nm in size (diameter), and it is difficult to form

20 pores of a cross-sectional size (or diameter) that is less than 7 nm. In other words, it is difficult to increase the figure of merit by producing nano-wires of a cross-sectional size (diameters) of 7 nm or less.

25 Accordingly, it is an object of the present invention to provide a thermoelectric conversion material and a thermoelectric conversion device of a novel structure by forming nano-wires of a thermoelectric material ~~to that~~ that have a narrower size

30 at a higher density than those conventionally

fabricated, ~~so as~~ to increase the figure of merit Z.

It is also an object of the present invention to provide a manufacturing method to easily produce such a thermoelectric conversion material ~~of a novel~~
5 ~~structure.~~

DISCLOSURE OF THE INVENTION

A first aspect of the present invention is a thermoelectric conversion material having a multi-
10 column structure, which comprises a porous body having columnar pores and a semiconductor material that can perform thermoelectric conversion, introduced into the pores of the porous body, characterized in that the porous body is formed by
15 removing the material forming the columns from a structure in which a plurality of columns of a column-forming material containing a first component are distributed in a matrix containing a second component being eutectic with the first component.

20 A second aspect of the present invention is a thermoelectric conversion material having a multi-column structure, characterized in that the column structure is obtained by the steps of: providing a porous body having a plurality of columnar pores,
25 which porous body is formed by removing the material forming the columns from a structure in which a plurality of columns of a column-forming material containing a first component are distributed in a matrix containing a second component that is eutectic
30 with the first component, introducing into the pores

a semiconductor material that can perform thermoelectric conversion; and then removing the porous body.

Preferably, the porous body is a thin film.

5 According to the present invention, it is possible to obtain nano-wires of a thermoelectric material ~~of which~~having cross-sectional size and density that cannot be achieved by the conventional anodization of aluminum.

10 According to the present invention, it is possible to obtain a structure comprising a plurality of columns and a matrix surrounding the columns, wherein the columns have a Seebeck coefficient at a room temperature larger than when the material
15 forming columns is in a bulk solid. The present invention also provides a thermoelectricity conversion device comprising, on a substrate, a structure, which comprises columns of a material and a matrix surrounding the columns, wherein the columns
20 have a Seebeck coefficient larger than that of the material in a bulk solid at room temperature, and the columns are electrically connected to electrodes; and the device generates current ~~flow~~ in response to external thermal change ~~of outside~~.

25 In the present invention, the porous body may be ~~subject~~subjected to a chemical treatment before the semiconductor material is introduced into the pores. The chemical treatment is desirably an oxidation treatment. Such a chemical treatment (oxidation
30 treatment) of the porous body allows the porous body

to be chemically stabilized. In some cases, the chemical treatment (oxidation treatment) can decrease the thermal conductivity of the porous body to thea level that is lower than that of anodized alumina, thereby ~~increase~~increasing the efficiency of the resulting thermoelectric conversion device.

In the present invention, preferably, the column-forming material is aluminum; the matrix is silicon or germanium; and the structure has 20 atomic% (inclusive) to 70 atomic% (inclusive) of silicon. ~~Alternatively, preferably the column-forming material is aluminum; the matrix is germanium; and the structure has 20 atomic% (inclusive) to 70 atomic% (inclusive) of germanium.~~

In the present invention, the main component of the porous body is silicon or germanium or a complex thereof, except for oxygen. Such a composition allows formation of nano-wires of a thermoelectric material, ~~of which~~having density and cross-sectional size that cannot be achieved by the anodization of aluminum.

The cross-sectional size of a column in the column-containing structure is desirably between 0.5 nm (inclusive) and 15 nm (inclusive). Such a cross-sectional pore size can provide a higher thermoelectric figure of merit.

The spacing of the columns in the column-containing structure is desirably between 5 nm (inclusive) and 20 nm (inclusive). Such spacing can

provide higher density of ~~nano-wires~~ of thermoelectric material nano-wires.

~~Part~~A part of the column-forming material is desirably a crystalline material, and the matrix is
5 desirably made of an amorphous material.

According to one aspect of the present invention, there is provided a manufacturing method of a thermoelectric conversion material of the present invention that comprises the steps of:
10 providing a structure in which columns of a column-forming material containing a first component are distributed in a matrix containing a second component that is eutectic with the first component; removing the column-forming material from the structure to
15 obtain a porous body; and introducing a semiconductor material into the pores of the porous body.

The method may have a further step of removing the matrix after the introduction step. The method may also have a step of chemically treating the
20 porous body after the removal step. The chemical treatment is desirably an oxidation treatment. The removal step is desirably etching. The introduction step is, preferably, electrodeposition.

The semiconductor material is, typically, but
25 not limited to, an alloy crystal composed of Bi, Sb, Te, and/or Se, such as BiSb or BiTe, and it may also be made from other various materials used as a thermoelectric conversion material in a bulk form, such as Si, SiGe, etc.

30 Investigating microstructures containing

aluminum, the inventors of the present invention found that in the preparation of an aluminum film on a substrate by using a film deposition method in a non-equilibrium state, such as sputtering, when
5 silicon and/or germanium are added in a predetermined ratio to aluminum, multiple aluminum columns are formed in silicon or germanium or a mixture thereof in a self-organizing manner. The inventors also found that when the film containing columnar aluminum
10 is immersed in a solution that dissolves aluminum, but not silicon or germanium or a mixture thereof, a porous body can be produced ~~of which~~ having a fine cross-sectional size and high pore density that cannot be achieved by anodization of aluminum.

15 The inventors found that the oxidation treatment of the produced porous body can change the material constituting the porous body to an oxide material.

 The inventors carried out an intensive study on the basis of the above findings to complete the
20 present invention.

 It is essential to use an aluminum-silicon (germanium) film in which the ~~amount~~ ratio of silicon (or germanium) to the total of aluminum and silicon (or germanium) is between 20 and 70 atomic%, because
25 ~~only in such a range,~~ a nano-structure having multiple columns of aluminum can be formed only in such a range. In other words, if the content of silicon (or germanium) is less than 20 atomic% of the total amount of aluminum and silicon (or germanium),
30 the cross-sectional size of aluminum columns

~~become~~becomes 15 nm or more ~~in cross-sectional size~~, while if the ratio of the amount of silicon (or germanium) to the sum amount of aluminum and silicon (or germanium) is more than 70 atomic%, an aluminum
 5 ~~columnar structure of aluminum~~ cannot be identified by typical scanning electron microscopes.

Introducing a semiconductor material by electrodeposition into such a porous body composed of silicon (or silicon oxide) or germanium (or germanium
 10 oxide) can ~~produce~~produce nano-wires with a small cross-sectional size (for example, not less than 0.5 nm and less than 15 nm) at a high density (for example, spacing not less than 5 nm and less than 20 nm). ~~Note~~It should be noted that the silicon (or
 15 silicon oxide) portion or the germanium (or germanium oxide) portion constituting the porous body may be removed after the formation of the nano-wires.

The structure from which the porous body is obtained (mother structure) will now be described.

20 The mother structure used in the present invention comprises a first component and second component, in which columns (column-forming material) containing the first component are surrounded by a matrix containing the second component. In this
 25 constitution, the mother structure desirably contains ~~the second component in a content~~ not less than 20 atomic% of the second component and less than 70 atomic% of the total of the first component and the second component.

30 The content, which is here referred to as the

ratio of the amount of the second component to the sum of the first component and second component, is preferably between 25 atomic% (inclusive) and 65 atomic% (inclusive), and more preferably between 30
 5 atomic% (inclusive) and 60 atomic% (inclusive).

~~Note~~It should be noted that the term "column-forming material" or "columns" refers to ~~these forming~~ substantially columnar forms, and the material may further contain the second component,
 10 and the matrix may further contain the first component. The column-forming material and the matrix surrounding it may contain small amounts of oxygen, argon, nitrogen and/or hydrogen.

The ratio can be determined quantitatively by,
 15 for example, inductively coupled plasma emission spectroscopic analysis. The values of the ratio described above are in atomic%. The range between 20 atomic% (inclusive) ~~to~~and 70 atomic% (inclusive) corresponds to the range between 20.65 wt%
 20 (inclusive) and 70.84 wt% (inclusive), with the atomic weight of Al being 26.982 and the atomic weight of Si being 28.086.

The first and second components are preferably a combination of materials having ~~an~~a eutectic point in
 25 at their phase diagram ~~of them~~ (so called eutectic materials). Specifically, the eutectic point is 300°C or higher, and preferably 400°C or higher. A preferable combination of the first and the second components may be a combination of Al (as the first

component) and Si (as the second component), a combination of Al (as the first component) and Ge (as the second component), or a combination of Al (as the first component) and $\text{Si}_x\text{Ge}_{1-x}$ ($0 < x < 1$) (as the second
 5 component).

The cross-section of the column-forming material is circular or oval. In the structure, the columns are distributed in a matrix containing the second component. The cross-sectional sizes of the columns
 10 (for circular cross sections, diameters) can be controlled as a function of the composition of the structure (or the content of the second component), and ~~the~~their average size ~~of them~~ is between 0.5 nm (inclusive) and 50 nm (inclusive), and preferably
 15 between 0.5 nm (inclusive) and 20 nm (inclusive), and more preferably between 0.5 nm (inclusive) and 10 nm (inclusive). ~~In~~If the ~~case of an~~shape is oval or the like, the major axis is preferably ~~between~~in such ranges. Here, the "average size" ~~means that which is~~
 20 a size derived, directly from, or through computer image processing of, actual picture images of columnar portions observed by SEM imaging (~~about a~~ range of about 100 nm by 70 nm). The lower limit of the average cross-sectional size for practical use is
 25 1 nm or larger, or several nm or larger.

The center-to-center distance of the columns, $2R$ is between 2 nm (inclusive) and 30 nm (inclusive), ~~and~~ preferably between 5 nm (inclusive) and 20 nm (inclusive), and more preferably between 5 nm
 30 (inclusive) and 15 nm (inclusive). ~~Note~~It should be

noted that the lower limit of the center-to-center distance $2R$ should be determined at least such that the columns have adequate spacing, so that they do not contact ~~with~~ each other.

5 The structure is preferably ~~one in the form of a~~
~~film-form, and in.~~ In this case, the columns are
distributed in a matrix containing the second
component where the columns are substantially
perpendicular to the film plane. There is no
10 specific limitation on the thickness of the film, and
the thickness may be between 1 nm and 100 μm .
Considering processing time, etc., the practical
thickness is between 1 nm and 50 μm . Preferably, a
film of 300 nm or thicker still has ~~columnar~~ column-
15 containing structure.

 The structure is preferably ~~one in the form of a~~
~~film-form~~, and may be formed on a substrate. The
substrate may be, but is not limited to, an insulator
substrate, such as quartz glass, a semiconductor
20 substrate, such as a silicon substrate, gallium
arsenide substrate or indium phosphide substrate, or,
if the structure can be formed on a metal substrate
or a substrate (a support matrix), a flexible
substrate (of polyimide, for example).

25 The structure can be fabricated using a film
deposition method conducted ~~in a~~ under non-equilibrium
~~condition~~ conditions. Such a film deposition method
is preferably sputtering, but any ~~of~~ other film
deposition ~~methods for forming~~ method that can be used

to form a material ~~in~~under any non-equilibrium ~~condition~~conditions can be used, including resistance heating evaporation, electron-beam evaporation (EB evaporation) or ion plating.

5 In the case of sputtering, ~~it may be~~ magnetron sputtering, RF sputtering, ECR sputtering or DC sputtering. ~~In the case of sputtering, the~~ may be used. Also, film deposition is performed typically in an argon atmosphere with a pressure in a reactor
10 on the order of 0.01 Pa to 1 Pa. ~~In the sputtering,~~ two ~~two~~ individual material targets, or a first material target and a second material ~~target~~target, may be used, ~~or alternatively.~~ Alternatively a material target ~~can be used which~~ that contains the
15 first material and second material that are sintered ~~with~~at a predetermined ratio can be used.

The structure ~~formed on~~ a substrate is formed ~~in~~ at a substrate temperature ~~of substrate~~ between 20°C (inclusive) and 300°C (inclusive), ~~and preferably~~
20 between 20°C (inclusive) and 200°C (inclusive).

Removing the column-forming material from the structure (by wet etching or dry etching) produces a porous body that contains multiple columnar pores. The etching only has to selectively remove the
25 column-forming material, and the etchant is preferably an acid, such as phosphoric acid, sulfuric acid, hydrochloric acid or nitric acid. The pores in the porous body produced by the removal are preferably isolated from each other or not connected

to each other.

The method for fabricating the porous body from the structure desirably has: a step of providing the structure containing a first component and a second
5 component, in which the column-forming material containing the first component ~~are~~is surrounded by a matrix containing the second component, and the ~~structure contains content of~~ the second component ~~at in the structure is~~ such that a ratio ~~that of~~ the
10 amount of the second component to the sum of the first component and second component ~~being is~~ is between 20 atomic% (inclusive) and 70 atomic% (inclusive); and a step of removing the column-forming material from the structure.

15

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram of a thermoelectric conversion material according to the present invention;

20 Fig. 2 is a process flow chart of a manufacturing method of a thermoelectric conversion material of the present invention;

Fig. 3 is a process flow chart of another manufacturing method of a thermoelectric conversion
25 material of the present invention;

Fig 4 illustrates a manufacturing method of a thermoelectric conversion material according to the present invention;

Fig. 5 is a schematic diagram of a thermal
30 conversion material of Example 1;

Fig. 6 is a schematic diagram of a thermal conversion material of Example 2;

Fig. 7 is a schematic diagram of a thermal conversion material of Example 3;

5 Fig. 8 is a schematic diagram of an exemplary thermoelectric conversion device employing a thermoelectric conversion material of the embodiments and examples of the present invention; and

10 Fig. 9 is an exemplary cross-section view of anodized alumina in the prior art with the pore spacing-~~of pores~~ being 10 nm or less.

BEST MODE FOR CARRYING OUT THE INVENTION

Embodiments of the thermoelectric conversion materials and manufacturing methods thereof according to the invention will now be described with reference to the accompanied drawings.

~~{Structure of thermoelectric conversion material}~~ Thermoelectric Conversion Material

20 Fig. 1 is a schematic diagram of an exemplary thermoelectric conversion material according to the embodiment. In this example, a thermoelectric conversion material is shown in which quantum wires (hereinafter, referred to as nano-wires) of a thermoelectric material having cross-sectional sizes of several nm (nanometers) to several tens nm are formed in the pores on a substrate. In Fig. 1, the reference numeral 11 refers to a film form of a thermoelectric conversion material; ~~the~~ reference
30 numeral 12 refers to a thermoelectric material formed

as nano-wires constituting the thermoelectric conversion material 11 (hereinafter, referred to as the nano-wire(s) if necessary); ~~the~~ reference numeral 13 refers to a substrate; and ~~the~~ reference numeral
5 14 refers to a porous body.

The nano-wires 12 are provided in the porous body 14. As shown in Fig. 1, the nano-wires 12 are separated from each other by the porous body 14, and are provided perpendicularly, or substantially
10 perpendicularly, to the substrate 13. The shape of the nano-wires 12 is columnar, as shown in Fig. 1. The diameter of the nano-wires 12 (the average diameter of nano-wires 12 viewed from the film surface) is between 0.5 nm (inclusive) and 15 nm (not
15 inclusive), and the spacing of the nano-wires 12 (the average center-to-center distance of the nano-wires viewed from the film surface) is between 5 nm (inclusive) and 20 nm (not inclusive).

The porous body 14 constituting the
20 thermoelectric conversion material 11 is formed by removing the column-forming material containing a first component distributed in a matrix containing a second component ~~that~~, which is eutectic with the first component. The column-forming material
25 containing the first component consists ~~of~~, for example, of a material that contains aluminum as the main component. The matrix containing the second component ~~being~~, which is eutectic with the first component, for example, is germanium or silicon or a
30 mixture of germanium and silicon.

The material of the porous body 14 preferably contains silicon (or silicon oxide) or germanium (or germanium oxide) as the main component. Alternatively, it may contain a mixture of silicon and germanium (or oxide of the mixture) as the main component. The material of the porous body 14 desirably contains silicon or germanium (or oxide thereof) as the main component, and may contain several to several tens atomic% of aluminum (Al), argon (Ar), nitrogen (N) and/or hydrogen (H).

While the material of the porous body 14 is preferably amorphous, it may ~~contains~~contain a crystalline material.

The material constituting the nano-wires is typically an alloy crystal consisting of Bi, Sb, Te and/or Se, such as Bi, BiSb or BiTe, but it is not limited thereto. Rather, it may be any one of various materials that are conventionally used as a thermoelectric conversion material in a bulk form.

In Fig. 1, the thermoelectric material 11 is not limited to the above -described configuration. Its ~~and may have a configuration~~ may be formed after removing the porous body 14 separating the thermoelectric material 12.

~~{Manufacturing method of thermoelectric conversion material}~~Method of Thermoelectric Conversion Material

Manufacturing methods of the thermoelectric conversion material according to the present invention ~~is~~are described below.

Fig. 2 is a process flow chart of an embodiment

of ~~the manufacturing method of the~~ thermoelectric conversion material manufacturing method. The manufacturing method shown in Fig. 2 has steps (a) to (c) as follows:

5 (a)÷ a step of providing a structure in which columns of a material containing a first component are distributed in a matrix containing a second component ~~that~~, which is eutectic with the first component; then

10 (b)÷ a step of removing the column-forming material from the structure to obtain a porous body; and then

 (c)÷ a step of introducing a semiconductor material into the pores of the porous body.

15 Fig. 3 is a process flow chart of another embodiment of ~~the~~ a method for manufacturing ~~method of~~ the thermoelectric conversion material:

 (a)÷ a step of providing a structure in which columns of a material containing a first component
20 are distributed in a matrix containing a second component ~~that~~, which is eutectic with the first component; then

 (b)÷ a step of removing the column-forming material from the structure to obtain a porous body;

25 (c)÷ a step of chemically treating (for example, oxidizing) the porous body; and then

 (d)÷ a step of introducing a semiconductor material into the pores of the porous body.

 A manufacturing method of the thermoelectric
30 conversion material will now be described more

specifically with reference to the drawings.

Fig. 4 illustrates an exemplary manufacturing process of a thermoelectric conversion material of this embodiment. Steps (a) to (c) are described one
5 by one.

Step (a): A structure in which columns of a material containing a first component 41 are distributed in a matrix containing a second component ~~44~~that 44, which can ~~form~~be eutectic with the first
10 component ~~41~~41, is provided.

Here, for example, aluminum (first component 41) and silicon (or germanium) (second component 44) are provided to form columns in a matrix. Then, a structured film of a mixture 43 (aluminum-silicon
15 mixture film or aluminum-germanium mixture film) is formed on a substrate 42 by using a method such as sputtering that can produce a film in a non-equilibrium state.

When an aluminum-silicon mixture film (or
20 aluminum-germanium mixture film) 43 is formed by using such a method, the aluminum and silicon (or germanium) form ~~an~~a eutectic structure in a metastable state in which the aluminum component separates and forms a nano-structure containing
25 multi-columns of several nm in the matrix in a self-organizing manner. Such aluminum columns are in a shape of a circular cylinder ~~of~~with a diameter between 0.5 nm (inclusive) and 15 nm (not inclusive),
and the column spacing is between 5 nm (inclusive)
30 and 20 nm (not inclusive).

~~In~~The silicon (or germanium) content in the aluminum-silicon mixture film (or aluminum-germanium mixture film) 43, ~~silicon (or germanium)~~43 is ~~contained~~ in a range of 20-70 atomic% of the total
 5 content of aluminum and silicon (or germanium) in the film ~~and~~, preferably between 25 and 65 atomic%, and more preferably between 30 and 60 atomic %. Silicon content in such a range allows formation of the aluminum-silicon mixture film (or aluminum-germanium
 10 mixture film) 43 in which columnar aluminum is distributed in a matrix of silicon (or germanium).

Here, the ratio of silicon to aluminum is represented by "atomic%" (atom% or at%), ~~that is,~~ i.e., a ratio of the number of silicon (or
 15 germanium) atoms to that of aluminum. Such ~~atomic%~~ ratio is obtained by a quantitative analysis of silicon (or germanium) and aluminum in the aluminum-silicon mixture film (or aluminum-germanium mixture film) 43, for example, by using inductively coupled
 20 plasma emission spectroscopic analysis (ICP).

Step (b): Then, the column-forming material is removed.

Here, for example, aluminum, the column-forming material in the aluminum-silicon mixture film (or
 25 aluminum-germanium mixture film) 43~~43~~, is etched away with phosphoric acid to form pores 46 in the matrix (here, silicon or germanium). This produces a porous body 45 on the substrate 42.

The pores 46 in the porous body 45 have a
 30 spacing from 5 nm (inclusive) to 20 nm (not

inclusive) and ~~its~~their cross-sectional size is from 0.5 nm (inclusive) to 15 nm (not inclusive).

The etching solution can be a solution of an acid, such as phosphoric acid, sulfuric acid,
 5 hydrochloric acid or chromic acid~~that~~, which dissolves aluminum, but hardly dissolves silicon or germanium. However, it may be an alkaline solution, such as an aqueous sodium hydroxide, as long as it does not have an adverse effect on the pore formation
 10 by etching,~~and thus~~. Thus, the etching solution should not be limited to specific types of acid or alkali. A mixture of acid solutions or alkaline solutions may also be used. The etching conditions,
 such as solution temperature, concentration and time,
 15 can be selected in a suitable manner depending on the porous body to be produced.

Step (c): A thermoelectric material (semiconductor material) 47 is introduced into the pores of the porous body produced by the removal
 20 step. Thus, the thermoelectric material 47 becomes nano-wires.

In this step, the porous body is filled with the thermoelectric material 47. For example, Bi or BiTe is filled ~~in to~~into the pores by electrodeposition.
 25 The thermoelectric material 47 is typically BiSb or BiTe~~having~~, which inherently has a high thermoelectric figure of merit~~inherently, but not limited to them~~. However, the material should not be so limited, and other various material may be
 30 used other materials that are used as thermoelectric

conversion materials in a-bulk form may be employed.

The method for filling the pores with the material is preferably electrodeposition, ~~and.~~ The pores may also be filled using a catalytic reaction method or VLS.

~~{Configuration of thermoelectric conversion device}~~
Thermoelectric Conversion Device

Fig. 8 is a schematic diagram of an exemplary thermoelectric conversion device of this embodiment.

10 Here, the "thermoelectric conversion device" ~~means~~ is either a thermoelectric generating device that converts heat to electricity, or a thermoelectric cooling device that provides a cooling effect by the current flowing therethrough. Fig. 8 shows an

15 example of such a thermoelectric generating device. The thermoelectric generating device of the present invention comprises a section of p-type thermoelectric conversion material 103 and a section of n-type thermoelectric conversion material 105.

20 Either thermoelectric conversion material section comprises a plurality of nano-wires (102 or 104) and a porous body 101. Fig. 8 shows only a pair of a p-type thermoelectric conversion material section 103 and an n-type thermoelectric conversion material

25 section 105. However, a typical configuration of the device has a plurality of ~~thesuch~~ such pairs arranged in series.

Here, a higher temperature electrode 108 and lower temperature electrodes 107 and 106 are not

30 supported on support plates. However typical

electrodes are desirably supported on a support plate.

Examples

The present invention will now be described
5 ~~specifically with~~by providing specific examples.

Example 1

In this example, a thermoelectric conversion material was produced, in which the porous body having the columnar pores was amorphous silicon, and
10 the semiconductor filled into the pores was BiTe.

First, an aluminum-silicon mixture film of about 200 nm thick containing 37 atomic% of silicon to the total of aluminum and silicon was formed by magnetron sputtering on a silicon substrate, on which 20 nm of
15 tungsten was deposited as an electrode for electrodeposition of BiTe (thermoelectric material). As a target, a six 15-mm square silicon chips are placed on a circular aluminum target of 4 inches in diameter (101.6 mm). Sputtering conditions employed
20 were such that a supply was used with an Ar flow of 50 sccm, a discharging pressure of 0.7 Pa and input power of 1 kW. The substrate temperature was room temperature (25°C).

The aluminum-silicon mixture film thus obtained
25 was observed by an FE-SEM (Field Emission-Scanning Electron Microscope). When the surface was viewed from above at an angle, it was found that round ~~columns of aluminum~~ columns surrounded by the silicon matrix were arranged two-dimensionally, as shown in
30 (a) of Fig. 4. The diameter of the aluminum column-

forming material ~~of aluminum~~ was 5 nm, and the average column spacing (center-to-center distance) ~~of them~~ was 8 nm. The FE-SEM observation of the cross-section shows that the ~~columns of aluminum~~ columns
 5 were isolated from each other.

Then, the aluminum-silicon mixture film thus fabricated was ~~immerses~~ immersed in 98% concentrated sulfuric acid for 24 hours to selectively etch away only the aluminum column-forming material ~~of aluminum~~
 10 so that pores were formed. As a result, a porous body was produced that consists of a material containing silicon as the main component, except for oxygen. The surface of the pores was oxidized.

The porous body consisting of a matrix
 15 containing silicon as the main component (the aluminum-silicon mixture film that had been subjected to the etching with concentrated sulfuric acid) was observed by the FE-SEM. The surface viewed from above at an angle had pores surrounded by the silicon
 20 matrix, arranged two-dimensionally, as shown in (b) of Fig. 4. The diameter of the pores was 5 nm, and the average spacing of ~~them~~ the pores was 8 nm.

Then, BiTe (semiconductor material) was filled into the pores of the porous body containing silicon as the main component. Here, a solution of 1 mol/l
 25 nitric acid dissolving Bi and Te therein was used for the electrodeposition of BiTe. The electrodeposition was performed in the solution with an Ag/AgCl reference electrode ~~of Ag/AgCl~~ at -1.0 V. Then, BiTe
 30 ~~pretruded~~ protruding from the pores ~~werewas~~ was polished

away.

The BiTe nano-wires thus fabricated in the porous body ~~was~~were observed with ~~an~~the FE-SEM to show that the substrate surface viewed from above at an angle had BiTe nano-wires 57 arranged two-dimensionally surrounded by the porous body 54 consisting of silicon as the main component, in a thermoelectric conversion material 53 formed on the substrate 52 shown in Fig. 5. ~~Viewed from a section,~~
 10 ~~the nano-wire 57 had a form of column.~~The nano-wires 57 were observed in a cross-section to have a columnar form. The average diameter of the nano-wires 57 was 5 nm, and the average center-to-center distance of the adjacent nano-wires 57 was about 8
 15 nm.

Example 2

In this example, a thermoelectric conversion material was produced, in which the main component of the porous body having the columnar pores was silicon
 20 oxide, and the semiconductor filled into the pores was BiTe.

First, an aluminum-silicon mixture film ~~of~~about 200 nm thick containing 37 atomic% of silicon to the total of aluminum and silicon was formed by magnetron
 25 sputtering on a silicon substrate, on which 20 nm of tungsten was deposited as an electrode for electrodeposition of BiTe (thermoelectric material). As a target, ~~a~~six 15-mm square silicon chips are placed on a circular aluminum target of 4 inches in
 30 diameter (101.6 mm). Sputtering conditions employed

were such that a supply was used with an Ar flow of 50 sccm, a discharging pressure of 0.7 Pa and input power of 1 kW. The substrate temperature was room temperature (25°C).

5 The aluminum-silicon mixture film thus obtained was observed with an FE-SEM (Field Emission-Scanning Electron Microscope) to find that the substrate surface viewed from above at an angle had a feature in which round ~~columns of aluminum~~ columns surrounded
10 by the silicon matrix were arranged two-dimensionally, as shown in (a) of Fig. 4. The diameter of the column-forming ~~material of aluminum~~ material was 5 nm, and the average spacing (center-to-center distance) of ~~them~~ the columns was 8 nm. The
15 FE-SEM observation of the cross-section showed that the ~~columns of aluminum~~ columns were isolated from each other.

Then, the aluminum-silicon mixture film thus fabricated was ~~immerses~~ immersed in 5wt% phosphoric
20 acid for 7 hours to selectively etch away only the aluminum column-forming material ~~of aluminum~~ so that pores were formed. At ~~thethat~~ that point, the silicon matrix that ~~had been surroundings~~ surrounded the aluminum columns was oxidized. As a result, a porous
25 body was produced consisting of a material containing silicon oxide as the main component.

The porous body mainly consisting of silicon oxide was observed by the FE-SEM. The surface viewed from above at an angle had pores surrounded by the
30 silicon oxide matrix, arranged two-dimensionally, as

shown in (b) of Fig. 4. The diameter of the pores was 5 nm, and the average spacing of ~~them~~the pores was 8 nm. The FE-SEM observation of the cross-section showed that the pores were isolated from each other by the matrix mainly consisting of silicon oxide.

Then, BiTe (semiconductor material) was filled into the pores of the porous body containing silicon oxide as the main component. Here, a solution of 1 mol/l nitric acid dissolving Bi and Te therein was used for the electrodeposition of BiTe. The electrodeposition was performed in the solution with a reference electrode of Ag/AgCl at -1.0 V. Then, BiTe ~~pretruded~~protruding from the pores ~~werewas~~ polished away.

The BiTe nano-wires thus fabricated in the porous body ~~was~~were observed by the FE-SEM. When the surface of a thermoelectric conversion material 63 formed on the substrate 62 was viewed from above at an angle, it was shown that BiTe nano-wires 67 were arranged two-dimensionally surrounded by the porous body 64 consisting of silicon oxide as the main component, as shown in Fig. 6. ~~From observation of a section of the substrate, the nano-wire 67 had a form of column.~~The nano-wires 67 were observed to have a columnar shape. The average diameter of the nano-wires 67 was 4 nm, and the average center-to-center distance of the adjacent nano-wires 67 was about 8 nm.

Example 3

In this example, a thermoelectric conversion material was produced, in which the material of the porous body having the columnar pores was germanium, and the semiconductor filled into the pores was BiSb.

5 First, an aluminum-germanium mixture film of about 200 nm that contained 37 atomic% of germanium relative to the sum amount of aluminum and germanium was formed by magnetron sputtering, on a silicon substrate, on which tungsten of 20 nm thick had been
10 deposited ~~thereon~~ as the electrode for electrodeposition of BiSb (thermoelectric material). A target was used in which four 15-mm square germanium chips are placed on a circular aluminum target having a diameter of 4 inches (101.6 mm).
15 Sputtering conditions were employed where RF power supply was used with an Ar flow: 12 sccm, a discharging pressure: 0.05 Pa and input power: 60 W. The substrate temperature was room temperature (25°C).

The aluminum-germanium mixture film thus
20 obtained was observed with ~~an~~the FE-SEM, and it was then found that the substrate surface viewed from an upper side with a slant had a feature in which substantially circular column-forming ~~material of~~ aluminum ~~was~~material was arranged two-dimensionally
25 while surrounded by the germanium matrix, as shown in (a) of Fig. 4. The diameter of the ~~columns of~~ aluminum columns was 10 nm, and the average center-to-center distance of ~~them~~the columns was 15 nm.

Then, the aluminum-germanium mixture film that
30 contained 37 atomic% of germanium relative to the sum

amount of aluminum and germanium was ~~immerses~~immersed in 98% concentrated sulfuric acid for 24 hours to selectively etch away only the aluminum column-forming material ~~of aluminum~~ so that pores were
 5 formed. As ~~thea~~ result, a porous body was produced containing germanium as the main component.

The aluminum-germanium mixture film that had been ~~subjected to the etching~~etched with a concentrated sulfuric acid (the porous body
 10 consisting of material containing germanium as the main component) was observed by the FE-SEM, and it was then found that the substrate surface viewed from an upper side with a slant had a feature in which pores were arranged two-dimensionally while
 15 surrounded by the germanium matrix, as shown in (b) of Fig. 4. The diameter of the pores, $2r$, was 10 nm, and the average spacing of ~~them~~the pores was 15 nm. Thus, the porous body containing germanium as the main component was produced. The fabricated sample
 20 was subjected to X-ray diffraction analysis and found to be amorphous.

Then, a semiconductor material was filled into the porous body thus produced containing germanium as the main component. Here, BiSb was filled into the
 25 porous body to produce BiSb nano-wires in the porous body. ~~Here, electrodeposition~~Electrodeposition of BiSb was employed with a solution of dimethyl sulfoxide (DMSO) in which $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and SbCl_3 were dissolved. The electrodeposition was performed in
 30 the solution with an Ag/AgCl reference electrode ~~of~~

~~Ag/AgCl~~ at -1.0 V. Then, the BiSb portions ~~protruded~~protruding from the pores were polished away.

The BiSb nano-wires thus fabricated formed in
 5 the porous body ~~was~~were observed by the FE-SEM, and
 it was then found that the surface viewed from an
 upper side with a slant had a feature in which BiSb
 nano-wires 77 were arranged two-dimensionally while
 surrounded by the porous body 74 containing germanium
 10 as the main component, in a thermoelectric conversion
 material 73 formed on the substrate 72 shown in Fig.
 7. Viewed from a cross-section of the substrate, the
 nano-wire 77 had a columnar ~~form of column~~. The
 average diameter of the nano-wires 77 was 10 nm, and
 15 the average center-to-center distance of the adjacent
 nano-wires 77 was about 15 nm.

As described in the above examples, according to
 the present invention, when a semiconductor material
 (thermoelectric material) is filled into a porous
 20 body, which is formed by providing a structure in
 which columns of a material containing a first
 component are distributed in a matrix containing a
 second component that can ~~form~~be eutectic with the
 first component, and then ~~removing~~ the column-forming
 25 material is removed from the structure, ~~this allows~~
~~the formation of nano-wires of thermoelectric~~
 material nano-wires with a diameter between 0.5 nm
 (inclusive) and 15 nm (not inclusive) and high
 density (the center-to-center distance of the nano-
 30 wires less than 20 nm) can be formed.

The material constituting the porous body may be any one of the various materials, such as silicon or germanium.

Example 4

5 In this example, a thermoelectric generating device was produced in which BiTe was employed as an n-type thermoelectric material and BiSb was used as a p-type thermoelectric material.

 First, an aluminum-silicon mixture film of about
 10 2 μm that contained 50 atomic% of silicon relative to the sum amount of aluminum and silicon was formed by magnetron sputtering, on a silicon substrate having silicon oxide surface (a support plate), on which 20 nm of tungsten had been deposited. Then, the
 15 aluminum-silicon mixture film that contained 50 atomic% of silicon relative to the sum amount of aluminum and silicon was ~~immerses~~immersed in 5 wt% phosphoric acid for 8 hours to selectively ~~etchingetch~~
 20 ~~etch~~ only the aluminum column-forming material ~~of aluminum~~ so that pores were formed. As the result, a porous body was produced that consists of material containing silicon oxide as the main component. Then, BiTe (n-type thermoelectric material) was electrodeposited. Then, resist
 25 ~~patterns of resist~~ were formed by photolithography, and ~~patterns of the~~ n-type thermoelectric conversion material patterns were generated by dry etching. Using similar process steps, BiSb (p-type thermoelectric material) was electrodeposited on the
 30 porous body and the silicon substrate with silicon

oxide (a support plate) with 20 nm of tungsten deposited thereon; resist patterns ~~of resist~~ were formed by photolithography; and ~~patterns of the p-type thermoelectric conversion material~~ patterns were
 5 generated by dry etching. The silicon substrate with silicon oxide, on which the p-type thermoelectric material is formed, and the silicon substrate with silicon oxide, on which the n-type thermoelectric material is formed, are attached together to form a
 10 thermoelectric conversion device, as shown in Fig. 8.

A thermoelectric conversion material employing a thermoelectric conversion material obtained by the above embodiments and examples will be described with reference to Fig. 8. A thermoelectric conversion
 15 device shown in Fig. 8, like known thermoelectric conversion devices in bulk form, is used for: a device, such as a cooler or thermal controller, which performs both cooling and heating where current flowing through a material causes heat generation at
 20 one end of the material and heat absorption at the other end, because of a Peltier effect; and a device, such as thermoelectric generator, which ~~generate~~ generates an electromotive force (thermoelectromotive force) by providing a
 25 temperature difference across a material (this is the opposite effect to that of the one mentioned above one).

In Fig. 8, the thermoelectric conversion device is embodied as ~~ana~~ a unit ~~composing~~ composed of multiple
 30 devices (π -type devices) connected in series, with

each π -type device consisting of: a thermoelectric conversion material section 103 having nano-wires 102 of a p-type semiconductor material (thermoelectric material) formed in a porous body 101 (hereinafter, referred to as a "p-type material section" 103); and a thermoelectric conversion material section 105 having nano-wires 104 of an n-type semiconductor material (thermoelectric material) formed in a porous body 101 (hereinafter, referred to as an "n-type material section") 105. In Fig. 8, reference numeral 106 refers to an electrode provided on one end of the p-type material section 103 (hereinafter, referred to as lower temperature-side); reference numeral 107 refers to an electrode provided on one end of the n-type material section 105 (hereinafter, referred to as lower temperature-side); and reference numeral 108 refers to an electrode provided on the other ends of the material sections 103 and 105.

In the case where the thermoelectric conversion device is ~~applied to a device that uses such an device~~used as a thermoelectric generating device, a plurality of the Π -type devices of Fig. 8 are connected in series. ~~Temperature~~The temperature difference between the upper electrode 108 and the lower electrodes 106 and 107 can cause the generation of electric power. ~~Here is illustrated the case where~~In Fig. 8, the upper electrode 108 is ~~in~~at a higher temperature while the lower electrodes is ~~in~~at a lower temperature, thereby generating an

electromotive force between the lower electrodes 106 and ~~107~~107, with the lower electrode 106 being positive and the lower electrode 107 being negative. The thermoelectric conversion device can also be used
5 as a cooling device, in which the electrode 106 is connected to a negative terminal of a power supply and the electrode 107 is connected to a positive terminal of the power supply, and current flowing therethrough can cause heat absorption from the upper
10 electrode 108 in Fig. 8. Thus, cooling around the upper electrode 108 can be performed. Such a thermoelectric conversion device can have a higher thermoelectric conversion figure of merit Z than conventional thermoelectric conversion devices.

15 ~~Note that the~~The present invention is not limited the embodiments, examples and applications illustrated above, but those skilled in the art can vary and modify them based on the ~~description of the~~ claims without departing from the gist of the present
20 invention. Such variations and modifications are also ~~in~~within the scope of the present invention.

As described in the above examples, according to the present invention, when a semiconductor material (thermoelectric material) is filled into a porous
25 body, which is formed by providing a structure in which columns of a material containing a first component are distributed in a matrix containing a second component that can ~~form~~be a eutectic with the first component, and then removing the column-forming
30 material from the structure, ~~this allows the~~

~~formation of~~ nano-wires of thermoelectric material
with a diameter between 0.5 nm (inclusive) and 15 nm
(not inclusive) and high density (the spacing of the
nano-wires less than 20 nm). ~~A thermoelectric~~
5 ~~conversion device~~ can be formed. An apparatus
employing such a thermoelectric conversion device can
also be provided. The present invention can also
provide a ~~production method allowing~~ that allows an
easy production of the thermoelectric conversion
10 ~~device.~~



ABSTRACT

A thermoelectric conversion material and a thermoelectric conversion device having a novel structure ~~of~~with an increased figure of merit are provided by forming nano-wires of thermoelectric material in a smaller cross-sectional size. The thermoelectric conversion material comprises nano-wires obtained by introducing a thermoelectric material (semiconductor material) into columnar pores of a porous body. The porous body is formed by providing a structure in which columns of a column-forming material containing a first component (for example, aluminum) are distributed in a matrix containing a second component (for example, silicon or germanium or a mixture of them) being eutectic with the first component, and then removing the column-forming material from the structure. The average diameter of the nano-wires of the thermoelectric material is 0.5 nm or more and less than 15 nm, and the spacing of the nano-wires is 5 nm or more and less than 20 nm.